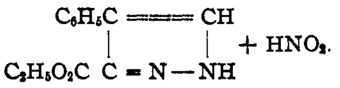


$$\begin{array}{lll} & C_6H_5C = & CH \\ & \quad | & \ \ | \quad + HNO_2. \\ C_2H_5O_2C & C = N - & NH \end{array}$$

The reaction was also tried in ligroin and in ether at the lowest temperature at which it would take place. In each oxides of nitrogen appeared soon after the reaction started and the only product was the pyrazol derivative.

Summary.

1. Four methods were tried for making cyclopropane derivatives having one ketonic and one carboxyl group in combination with the ring: decomposition of a ketonic cyclopropane diacid, eliminating hydrogen bromide from a γ-bromo-ketonic acid, removing bromine from an α,γ-dibromo ketonic acid, and decomposing a pyrazoline-ketonic ester. All these methods gave cyclic compounds, but only the last could be used for preparing a cyclopropane derivative.

2. Reagents that combine readily with α,β-unsaturated ketones also combine with this type of cyclopropane derivatives. The addition products are open chained saturated compounds.

3. Diazo-acetic ester readily combines with nitro-styrene; but the product loses nitrous acid so easily that a pyrazol derivative is obtained instead of the nitro-pyrazoline which is first formed.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

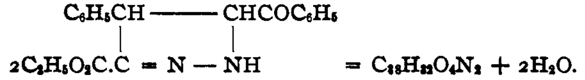
COLORED CONDENSATION PRODUCTS FROM KETONIC PYRAZOLINE DERIVATIVES.

BY E. P. KOHLER AND L. L. STEELE.

Received April 3, 1919.

The ketonic pyrazolines described in the previous paper give highly colored, fluorescent solutions in alcohol containing a trace of hydrochloric acid. We have isolated several of the products; they are high melting, sparingly soluble solids resembling the most brilliantly colored rhodamine dyes.

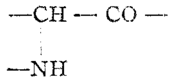
The pyrazoline derivative obtained by adding diazo-acetic ester to benzal-acetophenone gave a crimson product which was free from halogen. Its composition and molecular weight are represented by the formula $C_{38}H_{32}O_4N_4$. It is, therefore, formed in accordance with the equation



$$\begin{array}{ll} C_6H_5CH - & CHCOC_6H_5 \\ \quad\quad | & \ \ | \\ 2C_2H_5O_2C.C = N - & NH \end{array} = C_{38}H_{32}O_4N_4 + 2H_2O.$$

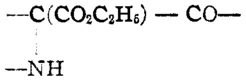
When the substance is allowed to remain in contact with a saturated solution of hydrochloric acid in alcohol, it takes up one molecule of the acid and one of water. The result is a yellow compound which readily loses both water and acid and reverts to the red product. In acetic acid the red compound combines with 2 molecules of water and forms a colorless compound which has the composition of the pyrazoline derivative but twice its molecular weight.

Similar products were obtained from all pyrazoline derivatives that had the grouping I, while a derivative which had the grouping II failed to give any color with hydrogen chloride.



$$\begin{array}{l}—CH—CO—\\ \;\;\vert\\ —NH\end{array}$$

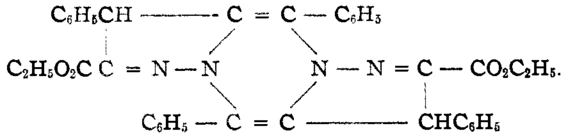
(I).



$$\begin{array}{l}—C(CO_2C_2H_5)—CO—\\ \;\;\vert\\ —NH\end{array}$$

(II).

The hydrogen α to carbonyl is, therefore, involved in the formation of the compound. This gives as a possible formula



Experimental Part.

When gaseous hydrogen chloride is passed into a concentrated solution of ethyl 4-phenyl-5-benzoyl-pyrazoline carboxylate-3 in alcohol, the solution turns red immediately but begins to fade again without depositing any solid material. If the solution is kept in ice-water while the gas is introduced, a crimson precipitate forms in small amount. When this is left in contact with the acid solution it redissolves and the color of the solution gradually fades. The red compound is evidently an intermediate product which has to be caught in passing.

The method of preparation finally adopted was as follows: hydrogen chloride was passed into 150 cc. of boiling methyl alcohol in which 20 g. of the ketonic pyrazoline was suspended as a fine powder. As soon as all of the pyrazoline had disappeared the precipitated crimson solid was filtered off and washed with alcohol. As no suitable solvent was found from which the substance could be recrystallized, it was purified by prolonged boiling with carbon disulfide. It was changed in the process from an impalpable powder to a mass of short, stout needles. After washing with ether these melted at 266–268°.

Calc. for $C_{38}H_{32}O_4N_4$: C, 75.0; H, 5.3. Found: C, 75.0; H, 5.2.

We failed to find any solvent in which the substance is sufficiently soluble for an accurate molecular-weight determination. Hot nitrobenzene dissolves about one g. of it per 100 g. of solvent and if this solution is allowed to cool without disturbance it generally retains the solute for several hours. The molecular weight found by freezing a somewhat more dilute solution than this was 525 instead of 608 calculated for the formula given.

The substance is so little soluble in alcohol and ether that it barely imparts a red tinge to the solutions. It is slightly soluble in benzene and carbon disulfide. The solutions are fluorescent; their color is a brilliant crimson-orange by reflected light, a rich purple by transmitted light. A specimen exposed to sunlight for 3 months, in a sealed tube, did not change either in color or melting point, but the dilute solutions in benzene acetone, and carbon disulfide soon faded to yellow in the light. The red compound is remarkably stable at high temperatures. In a vacuum it sublimes freely at about 400°.

Action of Hydrochloric Acid.—Hydrochloric acid was passed into a suspension of the red condensation product in alcohol. The red solid disappeared rapidly, the solution becoming at first greenish yellow and finally yellow. The alcohol, on evaporation, left a green powder which, after recrystallization from the same solvent, was obtained in yellow plates that melted to a red liquid at 258–259°.

Calc. for $C_{38}H_{35}O_5N_4Cl$: C, 68.8; H, 5.2; Cl, 5.4. Found: C, 68.9; H, 4.8; Cl, 5.9.

These results indicate that the yellow compound is formed by the addition of one molecule of water and one of hydrogen chloride to the condensation product. The substance gradually turns red both when heated by itself and when boiled with glacial acetic acid.

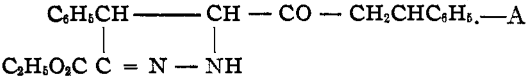
Action of Acetic Acid.—On protracted boiling with glacial acetic acid the red compound slowly dissolved and the solution finally became colorless. It was poured into water which precipitated a colorless product. By recrystallization from alcohol, this was obtained in small, colorless needles, which turned brown at about 170°, and melted to a clear brown liquid at 181°. The composition indicates that this compound is formed by the addition of 2 molecules of water to the red product.

Calc. for $C_{38}H_{36}O_6N_4$: C, 70.8; H, 5.6. Found: C, 70.8; H, 5.3.

Condensation Product from Ethyl 4-Phenyl-5(4-bromobenzoyl)-pyrazoline Carboxylate-3.—The condensation was carried out as with the bromine-free compound and the product purified in the same way. The brilliant purple-red needles melted at 268–270°.

Calc. for $C_{38}H_{31}O_4N_4Br$: C, 59.6; H, 3.9. Found: C, 60.1; H, 3.9.

Ethyl 4-Phenyl-5-benzalaceto-pyrazoline Carboxylate-3,



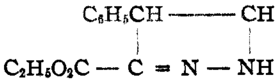
$$\begin{array}{lll} C_6H_5CH & \text{———} CH & - CO - CH_2CHC_6H_5 \\ \qquad | & \quad\ | & \\ C_2H_5O_2C\ C & = N - NH & \end{array}$$

.—A mixture of 10 g. of dibenzal-acetone and 9.8 g. of ethyl diazo-acetate was heated in ligroin at 50–70° for several hours, then allowed to remain at the ordinary temperature for several days, during which the pyrazoline derivative separated in light yellow plates. It was purified by recrystallization from alcohol in which it is only sparingly soluble. Its melting point was 164.5–165°. The yield was small.

Calc. for $C_{21}H_{20}O_3N_2$: C, 72.4; H, 5.8. Found: C, 72.1; H, 5.9.

When hydrogen chloride was passed into an alcoholic solution of the pyrazoline derivative it soon produced a deep blood-red color, but no pure product could be isolated. The dilute solutions were red by transmitted and green by reflected light.

Ethyl 4-Phenyl-5-aceto-pyrazoline Carboxylate-3,

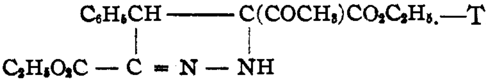


—A mixture of 7 g. of benzal-acetone and 5.7 g. of ethyl diazo-acetate was heated at 75–80° for two hours, during which 2.5 g. of solid product separated. This was washed with ether in which it was almost insoluble and recrystallized from alcohol. It separated in white needles melting at 127°.

Calc. for $C_{14}H_{16}O_3N_2$: C, 64.6; H, 6.2. Found: C, 64.8; H, 6.4.

A trace of hydrochloric acid in an alcoholic solution of the pyrazoline derivative produced an intense yellow color. More hydrochloric acid changed the color to orange and precipitated a small quantity of orange colored crystals. Dilute solutions of the condensation product were yellow by transmitted, and green by reflected light.

Ethyl 4-Phenyl-5-acetyl-pyrazoline Dicarboxylate-3,5,



—The pyrazoline derivative was prepared according to directions given by Buchner[1] but for some reason we obtained a product melting at 105–106° instead of 76° as given by Buchner. Our product was sparingly soluble in alcohol and crystallized in fine needles.

Calc. for $C_{17}H_{20}O_5N_2$: C, 61.4; H, 6.1. Found: C, 61.2; H, 6.0.

The substance is evidently a stereoisomer of the pyrazoline derivative obtained by Buchner, because when it was heated to 270–290° it lost nitrogen and gave the same pyrone ester which Buchner had obtained by heating the product melting at 76°.

Hydrogen chloride was passed in the usual way into an alcoholic solution of the pyrazoline derivative but failed to produce any color, and only unchanged substance separated when the solution was allowed to cool.

CAMBRIDGE, MASS.

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[1] *Ber.*, 35, 785 (1902).